ON THE QUANTUM THEORY OF ELECTRONIC IMPACTS[1]

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ABSTRACT

It is shown that the previous treatment of electronic collisions has been incomplete; the error consists in the neglect of terms in the solution which correspond to an interchange of the colliding electron with one of those in the atom. The corrected first order cross section for elastic collisions is evaluated by Dirac's method for atomic hydrogen and helium. The complete solution for hydrogen is set up by Born's method for hydrogen; it is shown that the elastic cross section becomes infinite, for low velocities, with the reciprocal of the velocity; it is further shown that the first order cross section reduces to that already obtained. For hydrogen this is a monotonically increasing function; for atoms with completely paired electrons the monotonic increase is broken by a minimum at velocities corresponding to about a volt; the higher the azimuthal quantum number of the paired valence electrons, the more marked the minimum, and the lower the voltage at which it occurs.

THERE are at present two methods of treating the collision of an electron with an atom. In the one calculation[2] one solves the transformation equation from the time to a set of constants of integration specifying the state of the atom and the components of momentum of the electron; and by choosing a solution which represents the atom initially in its normal state, and a free electron wave of unit intensity per unit time per unit area, one may obtain transition probabilities which give directly the cross section for an encounter of any specified type. In the second method[3] one obtains a solution of the stationary Schroedinger equation for the coupled system of atom and electron, combines the solutions to represent an incident wave of unit intensity per unit area impinging upon the unexcited atom, and interprets the scattered wave by means of a flux vector. In the former method one thus computes the rate of increase of the probability that the system is in the final state in question; in the second one finds the rate at which electrons leave the atom in this state; and since it follows from the normalization of the wave functions for this state that these two rates are equal,[4] the two methods are equivalent. The former method is more convenient for the estimation of first order cross sections; the latter for low velocity encounters, where the properties of the exact solution are important.

The first order problem has been solved explicitly for the collision of an electron with a hydrogen atom.[5] The cross section for elastic collision so

[1] For a preliminary account of this work see J. R. Oppenheimer, Proc. Nat. Acad. Sci. **14,** 261 (1928).

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[2] P. A. M. Dirac, Roy. Soc. Proc. **A114,** 243 (1927).

[3] M. Born, Zeits. f. Physik, **38,** 803 (1926).

[4] J. R. Oppenheimer, Phys. Rev. **31,** 66 (1928).

[5] M. Born, Goett. Nach. 146 (1926); W. Elsasser, Zeits. f. Physik, **45,** 522 (1927).

obtained is a monotonic function of the electronic velocity, and increases uniformly to a finite limit—the gas kinetic cross section—as the velocity is diminished. This calculation would indicate that for hydrogen there should be no Ramsauer effect, and no secondary maxima in the angular distribution of the scattered electrons.

Before the development of the quantum mechanics, Elsasser suggested[6] that these effects might be interpreted as the diffraction by the atom of the long de Broglie waves of the electron, and predicted that the elastic cross section should vanish with the fourth power of the electronic velocity. This argument is, however, incorrect. In the first place, as we shall show, the atom does not behave, even for slow collisions, as a rigid body: all the atomic characteristics are excited. In the second place Mensing showed[7] that, even for an especially favorable atomic model, the cross section does not vanish in the limit; this is because the refractive index within the atom is not, as in the optical case, nearly a constant, but varies instead with the reciprocal of the velocity. In the course of this work we shall see that the cross section does not become infinite faster than the reciprocal of the velocity; it is not possible to prove that it remains finite nor that it vanishes.

All of the work on collisions has, however, been incomplete. Analytically, this incompleteness is the result of neglecting, in the former method of treating the problem, transitions to states in which atomic and impacting electrons are interchanged; and, in the latter method, the excitation of the continuous spectrum. If one does not neglect these effects, he finds that, for a given atom, there is not one, but a series of elastic cross sections, corresponding to wave functions of differing symmetry in the orbital coordinates of the electrons in the atom and the colliding electron. Thus for hydrogen there are two cross sections, one for symmetric waves, one for waves antisymmetric in the coordinates of the two electrons. In general all cross sections approach, for high velocity encounters, those computed with neglect of the resonance terms; for low velocities there are characteristic deviations, which make the angular distribution of the scattered electrons irregular, and the total elastic cross section pass, in certain cases, through a minimum, instead of increasing monotonically with decreasing velocity.

In this paper we shall first compute by the former of the two methods the first order cross section for encounters with a hydrogen atom. We shall then set up the general equations for the collision by the second method, and show how the solutions are to be interpreted physically. We shall investigate the behavior of the elastic cross section for extremely low velocities; and we shall also show that the equations lead to a first order cross section identical with that found by the former method. We shall apply this to obtain the first order cross sections for hydrogen and helium, although these are of no quantitative significance; for the calculation itself shows the first approximation to be inadequate for low velocity encounters, and the full

[6] W. Elsasser, Naturwiss, **13**, 711, 1925.

[7] L. Mensing, Zeits. f. Physik, **45**, 603, 1927.

calculations appear impossible. We shall indicate, however, the physical predictions to be made on the basis of the theory, and obtain a few qualitative results for more complex atoms.

2. If we neglect the interaction of the atom and electron, we may describe the system by giving numerical values to six first integrals: the quantum numbers of the atom n, k, m, and the three electronic constants, ν, θ, ϕ, which are defined in terms of the cartesian components of the electronic momentum by the relations:

$$\nu = (2Mh)^{-1}[p_x{}^2 + p_y{}^2 + p_z{}^2] \; ; \quad \theta = \tan^{-1}(p_x{}^2 + p_y{}^2)^{1/2}/p_z \; ; \quad \phi = \tan^{-1}p_y/p_x, \quad (1)$$

where M is the reduced electronic mass. To each set of values of these six integrals we shall be able to assign two linearly independent wave functions; in particular these may be chosen respectively symmetric and antisymmetric in the coordinates of the two electrons. If they are so chosen, then a wave function initially symmetric will give rise, during the collision, only to symmetric waves; one initially antisymmetric will produce only antisymmetric waves: for the interaction energy is of course symmetric. If now one solves the transformation equation from this set of integrals to the time, he finds, for the first order cross sections[8]

$$\sigma_{nkm}(\nu',\theta,\phi) = (4\pi^2/h^2)\,|\,V_{\pm}(n,k,m,\nu',\theta,\phi)\,|^2 \qquad (2)$$

where ν' and n are connected with the initial value of ν, ν say, by the relation $\nu - \nu' - R + Rn^{-2} = 0$ where R is Rydberg's constant $2\pi^2 Me^4/h^3$. Here V_+ $(n, k, m, \nu', \theta, \phi)$ and $V_-(n, k, m, \nu', \theta, \phi)$ are the matrix components of the interaction energy for a transition from the initial wave function, which has

$$n=1, \quad k=0, \quad m=0, \quad \nu=\nu, \quad \theta=0$$

to a wave function with n, k, m, ν', θ, ϕ; and the wave functions are in the two cases respectively symmetric and antisymmetric.

These matrix components may readily be written down, although one cannot give explicitly the corresponding operator in coordinate space. If r_1 and r_2 are the vectors from the atomic center of gravity to the two electrons, and ψ_{nkm} the normalized hydrogen wave functions, and $\chi_{\nu\theta\phi}$ the normalized functions for the free electron, then the wave functions normalized to $d\nu$ are for the two cases respectively

$$\Psi^{\pm}_{nkm\nu\theta\phi} = 2^{-1/2}\{\psi_{nkm}(r_1)\chi_{\nu\theta\phi}(r_2) \pm \psi_{nkm}(r_2)\chi_{\nu\theta\phi}(r_1)\} \qquad (3)$$

Furthermore, the initial wave, properly normalized to represent a stream of unit intensity per unit area, is

$$2^{-1/2}\{\psi_{100}(r_1)\eta_\nu(r_2) \pm \psi_{100}(r_2)\eta_\nu(r_1)\} \qquad (4)$$

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[8] Here as in the following, the upper sign refers to the orbitally symmetric, the lower to the orbitally antisymmetric, solution.

with

$$\eta_\nu = (2\pi/\gamma) \cdot \chi_{\nu00} = (h/Mv)\chi_{\nu00} \qquad (5)$$

where v is the initial electronic velocity.

With

$$V(\boldsymbol{r}, \boldsymbol{r}') = -e^2/r + e^2/\,|\,\boldsymbol{r}\,|-\boldsymbol{r}'$$

the matrix components then become

$$2^{-1/2} \int d\boldsymbol{r}_1 \int d\boldsymbol{r}_2 \Psi_{nkm\nu'\theta\phi}^{\pm*} [V(\boldsymbol{r}_1, \boldsymbol{r}_2)\psi_{100}(\boldsymbol{r}_2)\eta_\nu(\boldsymbol{r}_1)$$

$$\pm V(\boldsymbol{r}_2, \boldsymbol{r}_1)\psi_{100}(\boldsymbol{r}_1)\eta_\nu(\boldsymbol{r}_2)] = f \pm g \qquad (6)$$

with

$$f(\nu', \theta, \phi) = \int d\boldsymbol{r}_1 \int d\boldsymbol{r}_2\, \psi_{nkm}^*(\boldsymbol{r}_1)\psi_{100}(\boldsymbol{r}_1)V(\boldsymbol{r}_2, \boldsymbol{r}_1)\chi_{\nu'\theta\phi}^*(\boldsymbol{r}_2)\eta_\nu(\boldsymbol{r}_2)$$

and

$$g(\nu', \theta, \phi) = \int d\boldsymbol{r}_1 \int d\boldsymbol{r}_2 \psi_{nkm}^*(\boldsymbol{r}_2)\psi_{100}(\boldsymbol{r}_1)V(\boldsymbol{r}_2, \boldsymbol{r}_1)\chi_{\nu'\theta\phi}^*(\boldsymbol{r}_1)\eta_\nu(\boldsymbol{r}_2)$$

so that we get for the elastic cross section

$$\sigma(\nu', \theta, \phi) = (4\pi^2/h^2)\,|\,f(\nu', \theta, \phi) \pm g(\nu', \theta, \phi)\,|\,^2 \qquad (7)$$

An obvious difficulty may perhaps be mentioned here. The functions ψ are all orthogonal to each other, and so are the functions χ; but the ψ's are orthogonal to the χ's only in the sense of continuous spectra:

$$\lim_{\Delta \to 0} \int d\boldsymbol{r} \int_\Delta d\nu \chi_{\nu\theta\phi}^*(\boldsymbol{r}) \cdot \psi_{nkm}(\boldsymbol{r}) \to 0$$

This is because ψ and χ satisfy different wave equations. The non-orthogonality is negligible for high velocities, but for slow encounters it may introduce a serious ambiguity. One may overcome this in principle by using in place of the χ's, the corresponding wave functions for the hyperbolic orbits of the hydrogen atom; and for high velocities this would give the same result as (7). But again for low velocities it would introduce a serious error into the first order cross section; for the two terms in the interaction energy which do in fact nearly neutralize each other would here be treated unsymmetrically; and the resulting cross section would turn out too large. We shall meet the same difficulty in a somewhat different form in 3.

By considering the secondary waves whose amplitude does not increase steadily with the time, one may solve the transformation equations correctly to a higher order; and the difficulty in the choice of proper orthogonal initial wave functions would then disappear. But this method is in practice less suited to the exact solution of the problem than that of Born.

3. The Schroedinger equation

$$[(h^2/8\pi^2 M)(\Delta_1+\Delta_2)+h(\nu-R)+e^2/r_1+e^2/r_2-e^2/\,|\,r_1-r_2\,|\;]\Psi=0 \qquad (8)$$

has solutions of the form[9]

$$\sum_{nkm}\{u_{nkm}(r_1)\psi_{nkm}(r_2)\pm u_{nkm}(r_2)\psi_{nkm}(r_1)$$

$$+\int_0^\infty d\nu'\sum_{km}\{u_{\nu'km}(r_1)\psi_{\nu'km}(r_2)\pm u_{\nu'km}(r_2)\psi_{\nu'km}(r_1)\} \qquad (9)$$

where the $\psi_{\nu'km}$'s are the hyperbolic wave functions for the hydrogen atom, with energy $h\nu'$, and normalized to $d\nu'$, and where the u's satisfy

$$[(h^2/8\pi^2 M)\Delta+h(\nu-R+Rn^{-2})]u_{nkm}(r)+K_{nkm}(r)=0 \qquad (10a)$$

and

$$[(h^2/8\pi^2 M)\Delta+h(\nu-R-\nu')-\nu')+e^2/r]u_{\nu'km}(r)+K_{\nu'km}(r)=0 \qquad (10b)$$

Here

$$K_{nkm}(r)=\sum_{n'k'm'}V_{nkmn'k'm'}u_{n'k'm'}(r)+\int_0^\infty d\nu'\sum_{k'm'}V_{nkm\nu'k'm'}(r)u_{\nu'k'm'}(r)$$

$$K_{\nu'km}(r)=\sum_{\nu'k'm'}V_{\nu'kmn'k'm'}(r)u_{n'k'm'}(r)+\int_0^\infty d\nu''\sum_{k'm'}\{V_{\nu'km\nu''k'm'}(r) \qquad (11)$$

$$+(e^2/r)\delta_{mm'}\delta_{kk'}\delta(\nu'-\nu'')\}u_{\nu''k'm'}(r)$$

and

$$V_{\nu'k'm'\nu km}^{n'\;n}(r)=\int dr'\psi_{\nu'k'm'}^{n'\,*}(r')V(r,r')\psi_{\nu km}^n(r')$$

If one considers a linear combination, ψ say, of the solutions (9), he sees that this involves some terms quadratically nonintegrable in r_1, some quadratically nonintegrable in r_2, and, for sufficiently large E, some quadratically integrable in neither r_1 nor r_2. Now for each pair of terms in ψ and ψ^* quadratically nonintegrable in r_1, there will correspond two waves in r_1-space, one approaching, the other receding, from the atom. One may then combine the solutions (9) with different u's in such a way that there is no ingoing wave in r_1-space to correspond to an excited or quadratically nonintegrable wave in r_2-space, and that the ingoing wave in r_1-space corresponding to the wave function of the unexcited atom in r_2-space represents a stream of electrons moving parallel to z, of $\frac{1}{2}$ electron per unit time per unit area. The incident wave will then have asymptotically the same form as that of

$$(2v)^{-1/2}\{\epsilon^{i\gamma z_1}\,\psi_{100}(r_2)\pm\epsilon^{i\gamma z_2}\,\psi_{100}(r_1)\} \qquad (12)$$

[9] Here as in the following, Σ_{nkm} indicates that the terms are to be summed over m from $-k$ to k, over k from 0 to $n-1$, over n from 1 to infinity. For Σ the term $n=1$ is omitted. Σ_{km} indicates summation over m as before, over k from 0 to infinity.

The corresponding solution (9) will then have, as we shall show, the asymptotic form

$$(2v)^{-1/2}\left\{\epsilon^{i\gamma z_1}\,\psi_{100}(r_2)\pm\epsilon^{i\gamma z_2}\,\psi_{100}(r_1)\right\}+\Gamma_{\pm}(v,\theta,\phi)\left\{(\epsilon^{-i\gamma r_1}/r_1)\psi_{100}(r_2)\right.$$

$$\pm(\epsilon^{-i\gamma r_2}/r_2)\psi_{100}(r_1)\right\}+\sum_{nkm}{}'D_{\pm}(n,k,m,v',\theta,\phi)\left\{(\epsilon^{-i\gamma_n r_1}/r_1)\psi_{nkm}(r_2)\right.$$

$$\pm\epsilon^{-i\gamma_n r_2}/r_2\cdot\psi_{nkm}(r_1)\right\}+\int_0^{\infty}dv''\sum_{km}F_{\pm}(v'',k,m,v',\theta,\phi)/r_1 r_2\cdot\left\{\epsilon^{-i(\gamma' r_1+\gamma'' r_2)}\right.$$

$$\pm\epsilon^{-i(\gamma' r_2+\gamma' r_1)}\right\}$$

with

$$\left.\begin{array}{l}\gamma_n=[\gamma^2-(8\pi^2 MR/h)(1-n^{-2})]^{1/2}\\\gamma'=2\pi(2Mv'/h)^{1/2}\\\gamma''=2\pi(2Mv''/h)^{1/2}\end{array}\right\}\quad;\quad\left.\begin{array}{c}v'=v-R(1-n^{-2})\\v'+v''+R-v=0\end{array}\right\}\qquad(13)$$

The constants D vanish for $v<3R/4$; the constants F vanish for $v<R$. The evaluation of the flux vector then gives for the cross section for elastic collision:

$$\sigma_0(v,\theta,\phi)=2v\left|\,\Gamma_{\pm}(v,\theta,\phi)\,\right|^2\qquad(14)$$

for the cross section for excitation[10] to the state n, k, m:

$$(h\gamma_n/\pi M)\left|\,D_{\pm}(n,k,m,v',\theta,\phi)\,\right|^2\qquad(15)$$

and for the cross section for ionization, in which the two electrons have the energies hv' and hv''

[10] In a recent paper (Proc. Nat. Acad. Sci. **13**, 800, 1927) the collision problem was considered, to obtain an estimate of the cross section for excitation when the electronic voltage approaches the resonance potential, in order to prove that in this limit the polarization of the excited light tends to vanish. In this treatment the continuous spectrum of the atom was neglected; and the treatment is therefore as it stands invalid. If one considers the continuous spectrum, one may in fact show that the polarization will tend to fall far below its value given by the momentum rules; it does not appear possible to show in general that it vanishes. Perhaps we may state the physical grounds for the failure of the momentum rule in an elementary way: when, as in the derivation of the momentum rules, the effect of the atom on the motion of the electron after the collision is neglected, only those electrons with vanishing angular momentum will have, in the limit, an appreciable chance of being near the atom; conversely, in this limit, the electron will have no appreciable chance of carrying away angular momentum; and this, since the electron initially had no angular momentum about the direction of the electron beam, at once gives, by the conservation theorem, the momentum rules. But when the influence of the atom on the final wave function for the electron is taken into account—and it is of capital importance in the limit when the electronic voltage approaches the resonance potential, the situation is changed; for now an electron with finite angular momentum can be near the atom; conversely the electron can now take up, and in general will take up, momentum from the atom; and thus excitations forbidden by the momentum rule will occur. It may be added that this modification does not affect at all the second part of the paper quoted, which is concerned with the anomalous polarization of the intercombination lines.

$$(\gamma'\gamma''h^2/2\pi^2M^2)\,|\,F_{\pm}(\nu',k,m,\nu'',\theta,\phi)\,|\,^2 \tag{16}$$

In each case there is a cross section corresponding to waves initially symmetric, and one corresponding to waves initially antisymmetric, in the orbital coordinates of the electrons. We shall consider this solution in detail for the case $\nu < \frac{3}{4}R$.

For this case the wave

$$\sum_{nkm}u_{nkm}(\mathbf{r}_2)\psi_{nkm}(\mathbf{r}_1)+\int_0^\infty dv'\ \sum_{km}u_{\nu'km}(\mathbf{r}_2)\psi_{\nu'km}(\mathbf{r}_1) \tag{17}$$

will involve only one set of waves quadratically nonintegrable in r_2. For both $K_{nkm}(\mathbf{r}_2)$ and $K_{\nu'km}(\mathbf{r}_2)$ vanish as $r_2\to\infty$, since the V's fall off at least with $1/r$, and the u's are bounded uniformly in r. Thus the equations for the u's take the asymptotic form

$$\begin{aligned}[\Delta+\lambda_n]u_{nkm}=0 \qquad & \lambda_n=(8\pi^2M/h)(\nu-R+Rn^{-2})\\ [\Delta+\lambda_{\nu'}+e^2/r]u_{\nu'km}=0 \ & \lambda_{\nu'}=(8\pi^2M/h)(\nu-R-\nu')\end{aligned} \tag{10c}$$

And for all the u's except u_{100} the parameter λ is negative; the corresponding solutions will therefore be uniformly quadratically integrable; only u_{100} will involve waves which extend to infinity.

Similarly, there will be only one set of waves quadratically nonintegrable in r_1. For in the first place all the functions for the discrete states, ψ_{nkm}, fall off exponentially. And although the functions $\psi_{\nu'km}$ are quadratically nonintegrable, the coefficients $u_{\nu'km}$ are uniformly bounded in ν and r_2 except in the immediate neighborhood of $\nu'=\nu$. To see this we may examine more closely the equations (10) for the u's. If we take the second term in the expression for $K_{\nu'km}$, we see that it is an improper integral; for in the nucleus for $\nu''=\nu'$, the term

$$\int d\mathbf{r}'\,|\,\psi_{\nu'km}(\mathbf{r}')\,|\,^2e^2/\,|\,\mathbf{r}-\mathbf{r}'\,|$$

does not exist. We may, however, modify the work to get rid of this difficulty. The physical reason for the modification will be made evident when we consider the interpretation of the waves. Let us expand the solution ψ in terms of the ψ_{nkm}'s, as before, but replace the $\psi_{\nu'km}$'s by the solutions $\phi_{\nu'km}$ of the differential equation

$$[(h^2/8\pi^2M)\Delta+h\nu'+(e^2/r)\epsilon^{-r/B}]\phi_{\nu'km}(\mathbf{r})=0 \tag{18}$$

where B is a large positive constant. Then

$$\lim_{B\to\infty}\phi_{\nu km}\to\psi_{\nu km}$$

$$\lim_{B\to\infty}\int d\mathbf{r}\,\psi_{nkm}^{*}(\mathbf{r})\phi_{\nu km}(\mathbf{r})\to 0$$

so that by going to the limit $B \to \infty$ in the final expressions for the cross sections, we shall obtain the solutions (9). For finite B the solutions will now have the $\phi_{\nu'km}$ in place of the $\psi_{\nu'km}$ in (9), the u's will be given by (10), and for the K's we shall have the proper integral

$$\int_0^\infty d\nu'' \sum_{k'm'} U_{\nu'km\nu''k'm'}(\mathbf{r}) u_{\nu''k'm'}(\mathbf{r}) \quad \text{with} \quad U_{\nu'km\nu''k'm'}(\mathbf{r})$$

$$= \int d\mathbf{r}' \phi_{\nu''k'm'}(\mathbf{r}') \phi_{\nu'km}(\mathbf{r}') \left\{ -e^2 / \left| \mathbf{r} - \mathbf{r}' \right| + (1 - \epsilon^{-r^1/B}) e^2 / r' \right\} \tag{19}$$

Now the inhomogeneous terms K will be bounded. And unless

$$\nu - R - \nu' = -R/e^2 \tag{20}$$

where l is integral, the inhomogeneous equations will have bounded solutions. But since

$$\nu - R - \nu' < -R/4$$

only for $l = 1$ will the homogeneous equation be soluble, and only for this value of ν' will the amplitude of the solution of the inhomogeneous equation become infinite. The integral in (17) thus has the form

$$\int_0^\infty d\nu' \sum_{km} L_{\nu'km}(\mathbf{r}_2) \phi_{\nu'km}(\mathbf{r}_1) + \int_{\nu-\epsilon}^{\nu+\epsilon} d\nu' \sum_{km} h^{-1} (\nu - \nu')^{-1} \phi_{\nu'km}(\mathbf{r}_1) \psi_{100}(\mathbf{r}_2)$$

$$\int d\mathbf{r}' \psi_{100}^*(\mathbf{r}') K_{\nu'km}(\mathbf{r}') \tag{21}$$

where L is a function bounded in ν' and r_2. Now the first term of (21) gives a wave in r_1 which is quadratically integrable, since it is expansible in terms of the ϕ's with uniformly bounded coefficients. The second term gives at once

$$-\kappa_{\nu km} \phi_{\nu km}(r_1 - \pi i / 2\gamma, \theta, \phi) \psi_{100}(\mathbf{r}_2) \tag{22}$$

with

$$\kappa_{\nu km} = 2\pi h^{-1} \int d\mathbf{r}' \, \psi_{100}^*(\mathbf{r}') \, K_{\nu km}(\mathbf{r}') \tag{23}$$

Now the ϕ's may be given asymptotically by

$$\phi_{\nu'km}(\mathbf{r}) = \phi_{\nu'km}(r, \theta, \phi) \sim (2/v)^{1/2} Y_{km}(\theta, \phi) \sin \left[\gamma r + \alpha(\nu', k) \right] \tag{24}$$

where θ and ϕ are the polar angles of the vector $\mathbf{r}$, the Y_{ps} are the normalized spherical harmonics of order p and degree s, and the α's are real constants depending upon B. Similarly

$$u_{100}(\mathbf{r}) \sim \sum_{km} Y_{km}(\theta, \phi) / r \cdot \left\{ B_{+km} \epsilon^{i(\tau_{km} + \gamma r)} + B_{-km} \epsilon^{i(\tau - km - \gamma r)} \right\} \tag{25}$$

with the B's and τ's real. As we shall show, the B_{-km} and τ_{-km} may be determined in terms of the B_{+km} and τ_{+km} by the wave equation (10a). (See (36) and (37)). Further the κ's are determined in these terms by (19) and (23). Finally the remaining u's are determined; for the corresponding homogeneous equations have no solution, and the inhomogeneous terms depend only on the B's and τ's and κ's. For the case $\nu < 3R/4$, then, the solution is completely given in terms of the two sets of constants B_{+km} and τ_{+km}; and these must be chosen to make the incident wave of the solutions (9) one of unit intensity per unit area:

$$B_{+km}\epsilon^{i\tau+km} \mp v^{-1/2}\kappa_{\nu km}\epsilon^{i\alpha(\nu,k)} = (2v)^{-1/2}\gamma^{-1}\delta_{m0}(k+1/2)\epsilon^{(k+1/2)\pi i} \qquad (26)$$

The scattered wave then becomes

$$\sum_{km}\Delta_{km}\left\{\epsilon^{-i\gamma r_1}/r_1 \cdot \psi_{100}(\mathbf{r}_2)Y_{km}(\theta_1,\phi_1) \pm \epsilon^{-i\gamma r_2}/r_2 \cdot \psi_{100}(\mathbf{r}_1)Y_{km}(\theta_2,\phi_2)\right\} \qquad (27)$$

with

$$\Delta_{km} = B_{-km}\epsilon^{i\tau-km} - B_{+km}\epsilon^{i\tau+km-(k+1)\pi i} \mp v^{-1/2}\kappa_{\nu km}\epsilon^{-i\alpha(\nu,k)} \qquad (28)$$

This yields at once the elastic cross section. Of this we have to show (a) that in the limit $v \to 0$ it grows in general with v^{-1}; and (b) that in first order it reduces to (7).

The physical interpretation of the waves (9), (13), is immediate. In spite of the fact that the atom cannot be excited or ionized by the collision without violation of the energy theorem, the wave functions for such excitation do not in general vanish identically; instead they fall off rapidly as the nonatomic electron recedes from the atom, so that the chance of finding the atom excited or ionized is only then considerable when another electron is in its immediate vicinity. The excitation is thus not permanent; during the collision the atom will make quantum jumps; but when the collision is over the atom will have returned to its normal state. The electron which is left in the normal state is not necessarily the same as was originally there; but since one has no way of distinguishing which was originally in the atom, it is physically meaningless to ask which has escaped.

The necessity for replacing the ψ's by the ϕ's in order to make the integral for the K's exist may be interpreted in this way: the hyperbolic wave functions $\psi_{\nu'km}$ are not a possible zero order approximation to the motion of the ejected electron; for this ejection only takes place when the atom is left neutral, and not ionized; and the hyperbolic wave functions do not approach, for infinite distance, a linear combination of the waves which represent the motion of an electron with the same energy in the field of a neutral atom. In the final results the limit $B \to \infty$ should exist.

Write

$$u_{100}(\mathbf{r}) = \sum_{km} y_{km}(r)Y_{km}(\theta,\phi) \qquad (29)$$

Then the equations for the y's are, with $\xi = \gamma r$,

$$(d/d\xi)(\xi^2 y_{km}'(\xi)) + [\xi^2 - k(k+1)]y_{km}(\xi) + \gamma^{-2}\xi^2 S_{km}(r) = 0 \qquad (30)$$

where

$$S_{km}(r) = \int d\phi \int d\theta \sin\theta Y_{km}^*(\theta,\phi) K_{100}(r,\theta,\phi)$$

and

$$K_{100} = V_{100100} u_{100} - \sum_{km} \kappa_{\nu km} V_{100\nu km} \psi_{100} + {\sum_{nkm}}' V_{100nkm} u_{nkm}$$

$$+ \int_0^\infty d\nu' \sum_{km} V_{100\nu'km} L_{\nu'km} \qquad (31)$$

The solutions of (30) which remain finite for $\xi = 0$ then satisfy

$$y_{km} = c_{+km} y_{+k}(\xi) + c_{-km} y_{-k}(\xi) + \overset{\circ}{I}_{km}(\xi) \qquad (32)$$

with

$$y_{+k}(\xi) = \xi^{-1/2} J_{k+1/2}(\xi) \; ; y_{-k}(\xi) = \xi^{-1/2} J_{-k-1/2}(\xi)$$

$$I_{km}(\xi) = \gamma^{-2} \int_\infty^\xi dx\, G_k(x,\xi) S_{km}(x) \qquad (33)$$

and

$$c_{-km} = - \lim_{\xi \to 0} [I_{km}(\xi) \cdot y^{-1}_{-k}(\xi)] \qquad (34)$$

and

$$G_k(x,\xi) = \begin{vmatrix} y_{+k}(x) & y_{+k}(\xi) \\ y_{-k}(x) & y_{-k}(\xi) \end{vmatrix} \cdot \begin{vmatrix} y_{+k}(x) & y_{-k}(x) \\ y'_{+k}(x) & y'_{-k}(x) \end{vmatrix}^{-1} \qquad (35)$$

We shall see (45), (47) that I exists and vanishes for $\xi \to \infty$. The solution (29) then behaves asymptotically like (25) with

$$B_{\pm km} = (2\pi)^{-1/2}\gamma^{-1}\{ \, |c_{+km}|^2 + |c_{-km}|^2 + 2|c_{+km}\, c_{-km}| \, \epsilon^{(k+1/2)\pi i \pm \pi i}$$

$$\sin[\arg c_{+km} - \arg c_{-km}]\}^{1/2} \qquad (36)$$

and

$$\sin \tau_{\pm km} = (2\pi\gamma B_{\pm km})^{-1/2}\{ \, |c_{+km}| \sin[\arg c_{+km}$$

$$\pm (k+1)\pi/2] + |c_{-km}| \cdot \sin[\arg c_{-km} \mp k\pi/2]\} \qquad (37)$$

The incident wave will thus represent a stream of unit intensity if $|c_{+km}|$ and arg c_{+km} are chosen so that (26) is satisfied. This shows that,[11] as $v \to 0$

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[11] Here, as in the following, A is a fixed positive constant independent of r, v, k, m.

$$\left| c_{+km} \right|^2 + \left| c_{-km} \right|^2 < A v^{-1} \tag{38}$$

We shall now show that

$$\left| c_{-km} \right| < A v^{1/2} \tag{39}$$

for the case that $V_0 = V_{100\,100} < A r^{-2-\epsilon}$ i.e., that the atom has no dipole moment in its normal state. For in the first place

$$\left| V_{100nkm} \right| < A/r \tag{40}$$

Further, by (10) and (38)

$$\left| u_{nkm} \right| < v^{-1/2} Q(r) \; ; \left| L_{\nu km} \right| < v^{-1/2} Q(r) \tag{41}$$

where the Q's are bounded uniformly in v, and are, as we have shown, quadratically integrable in r. Further, as we shall show (57)

$$\left| \kappa_{\nu km} \right| < v^{-1/2} A \; ; \; V_{100\nu km} < A/r \tag{42}$$

Finally

$$\left| V_0 u_{100} \right| < v^{-1/2} A r^{-2-\epsilon} \tag{43}$$

Thus by (31)

$$\left| S_{km} \right| < A v^{-1/2} r^{-1} \text{ for } v \leqq r_0 \tag{44}$$

$$\left| S_{km} \right| < A v^{-1/2} r^{-2-\epsilon} \text{ for } r > r_0 \tag{45}$$

But on the other hand it follows from the non-vanishing of the Wronskian and the expansions for the J's that

$$\lim_{\xi \to 0} \left[G_k(x,\xi)(y_{-k}(\xi))^{-1} \right] \begin{matrix} < A x \text{ for } x > x_0 \\ < A x^{2+k}(\ln x)^{\delta_{1k}} \text{ for } x \leqq x_0 \end{matrix} \Bigg\} \tag{46}$$

Hence

$$c_{-km} = \int_{\infty}^0 T_{km}(x)\,dx \tag{47}$$

with

$$\left| T_{km} \right| \begin{matrix} < A v^{-3/2} x^{1+k}(\ln x)^{\delta_{1k}} \text{ for } x \leqq x_0 \\ < A v^{-1/2+\epsilon} x^{-1-\epsilon} \text{ for } x > x_0 \end{matrix} \Bigg\}$$

From this we find, uniformly in v

$$\left| c_{-km} \right| < A v^{1/2+k}(\ln v)^{\delta_{1k}} \tag{48}$$

as announced.

To estimate the κ's we may note first that the ϕ's remain uniformly bounded as $v \to 0$, and approach

$$A_k J_{2k+1}\left[(2\pi e/h)(2Mr)^{1/2}\right] \cdot Y_{km}(\theta,\phi)$$

Thus the matrix components $U_{\nu' k' m' \nu k m}$ exist, and remain uniformly bounded as $v \to 0$, satisfying

$$| U | < A/r \tag{49}$$

Further, from (41)

$$| u_{nkm} | < A v^{-1/2} \; ; \; | L_{\nu k m} | < A v^{-1/2} \tag{50}$$

Thus

$$| \kappa_{\nu k m} | < A v^{-1/2} \tag{51}$$

as used in (43).

Hence from (27) we find, uniformly in k and m, that if the $|c_{+km}|$ and the arg c_{+km} are chosen to satisfy (26)

$$| \Delta_{km} | < A v^{-1} \tag{52}$$

Thus

$$| \Gamma_{\pm}(\nu, \theta, \phi) | < A v^{-1} \tag{53}$$

and (14) gives for the cross section

$$\sigma_0(\nu, \theta, \phi) < A v^{-1} \tag{54}$$

If we had neglected the continuous spectrum, we should have found instead that σ_0 approached in the limit a finite constant independent of θ and ϕ, so that scattering became uniform over all angles. But this result is of no physical significance; and since we have used the properties of the wave functions to obtain the lowest upper limit for σ_0 that they in general permit, we must conclude that in general the cross section grows in accordance with (54).

When we evaluate σ_0 in first order, we may introduce several simplifications. In the first place we may neglect the influence of the scattered wave on the incoming wave, as this would give a term of second order. We may thus satisfy (26) by setting

$$c_{+km} = (\pi/v)^{1/2} \delta_{m0}(k + \tfrac{1}{2}) \epsilon^{(k+1/2)\pi i} \tag{55}$$

Further we may replace the ϕ's by the ρ's, defined by

$$\rho_{\nu k m}(r) = \int d\phi \int \sin \theta d\theta Y_{km}{}^*(\theta, \phi) \chi_{\nu \theta \phi}(r) \tag{56}$$

(This amounts to setting $B = 0$), since the validity of the first order calculation depends upon neglecting the distinction between the ψ's and the χ's, and, as pointed out in 2, it is best to use the same functions for both electrons. (See further 4.) Finally we may evaluate K_{100} and $K_{\nu k m}$ by giving the u's their initial values

$$u_{\nu k m} = u_{nkm} = 0 \tag{57}$$

except

$$u_{100} = (2v)^{-1/2}\epsilon^{i\gamma z} = 2^{-1/2}\eta_\nu$$

Then (23) gives

$$\kappa_{\nu km} = 2^{1/2}\pi h^{-1} \int d\mathbf{r} \int d\mathbf{r}' \psi_{100}{}^*(\mathbf{r}')\psi_{100}(\mathbf{r})\eta_\nu(\mathbf{r}')\rho_{\nu km}{}^*(\mathbf{r})V(\mathbf{r}',\mathbf{r}) \qquad (58)$$

and with (28), (23), (25), and (30) we get

$$\Delta_{km} = -2\pi h^{-1}(2v)^{-1/2} \int d\mathbf{r} \int d\mathbf{r}' \,|\, \psi_{100}(\mathbf{r}) \,|^2 \eta_\nu(\mathbf{r}')\rho_{\nu km}{}^*(\mathbf{r}')V(\mathbf{r}',\mathbf{r})$$

$$\mp 2\pi h^{-1}(2v)^{-1/2} \int d\mathbf{r} \int d\mathbf{r}' \psi_{100}{}^*(\mathbf{r}')\psi_{100}(\mathbf{r})\eta_\nu(\mathbf{r}')\rho_{\nu km}{}^*(\mathbf{r})V(\mathbf{r}',\mathbf{r}) \qquad (59)$$

Thus with (56)

$$\Gamma_\pm(\nu,\theta,\phi) = 2\pi h^{-1}(2v)^{-1/2}\big[-f(\nu,\theta,\phi)\mp g(\nu,\theta,\phi)\big] \qquad (60)$$

which, with (14), gives

$$\sigma_0(\nu,\theta,\phi) = (4\pi^2/h^2)\,|\,f-g\,|^2 \qquad (61)$$

in agreement with (7).

4. The quantitative estimation of these cross sections has no very precise significance. For the ρ's are a very bad approximation to the wave functions for the aperiodic motion of the electrons; they are not orthogonal to the ψ_n's; and they give a cross section which remains finite for $v=0$, whereas the true cross section presumably becomes infinite with v^{-1}. This may be shown to depend upon the fact that the ρ's approach zero for $v=0$, whereas the ϕ's and presumably the true functions, do not. Nor can one overcome this difficulty by using the ψ's or the ϕ's for the ρ's; in the former case the flux vector does not exist, and in the second case it depends essentially, in the first order calculation, upon B, and does not approach a limit when $B\to\infty$. These difficulties would disappear in a complete solution, but at present they appear analytically inevitable.

The qualitative characteristics of σ_0 are easy to obtain. The first term f is

$$f(\nu,\theta,\phi) = f(\nu,\theta) = -(e^2/8\pi R)\big\{[1+\nu/R\cdot\sin^2\theta/2]^{-1} + [1+(\nu/R)\sin^2\theta/2]^{-2}\big\} \qquad (62)$$

and is just the term that gives Born's cross section. The second term cannot be written in closed form. For large v it is smaller than f, since

$$g < Av^{-5} \qquad (63)$$

whereas f falls off only with the inverse square of v. For $v=0$ we have directly

$$g_0 = g(0,\theta,\phi) = \int d\mathbf{r} \int d\mathbf{r}' \psi_{100}{}^*(\mathbf{r}')\big\{-e^2/r' + e^2/|\,\mathbf{r}-\mathbf{r}'\,|\big\}\psi_{100}(\mathbf{r})$$

$$= -3e^2/2\pi R = +6f(0,\theta) \qquad (64)$$

For fixed angle of deflection θ both f and g decrease monotonically with increasing v. Thus for each value of θ there is a value of v for which the two terms become equal. These values of v lie within a small range for which v corresponds to a few volts.

The symmetric cross section is always larger than Born's value. For large v it is nearly equal to this latter; for small v it is 49 times as great. It increases monotonically with decreasing v. The angular distribution of scattered electrons varies slowly with v, and there are no secondary maxima.

The antisymmetric cross section is much larger than Born's for $v=0$, and nearly equal to it for large v. But in the range in which the functions $f(\nu, \theta) - g(\nu, \theta)$ have their zeros, it will be smaller than Born's value; and because these values of v lie in a small range, the total cross section

$$\int d\phi \int \sin\theta d\theta \sigma_0(\nu,\theta)$$

has a minimum in this region. In this region also there are secondary maxima in the angular distribution of the electrons.

Had we taken for the normal state of the atom, a P or D, instead of an S, term, with wave function, say, respectively

$$\psi_{210} = \text{const } \epsilon^{-r/2a} r \cos\theta$$

$$\psi_{320} = \text{const } \epsilon^{-r/3a} r^2 (3 \cos^2\theta - 1)$$

we should obtain analogous results. But since in this case

$$g < A v^{-7}$$
$$g < A v^{-9} \tag{65}$$

for the two functions respectively, the second term will fall off more rapidly than for the S state, and the zeros of f-g will thus occur for lower values of v. And since they will also occur within a smaller range, the minimum in the total cross section will be more marked. Quite generally, the lower the position of the minimum, the sharper it will be. For θ enters the cross section only in the form $v \begin{pmatrix} \cos\theta \\ \sin\theta \end{pmatrix}$ so that, the lower the velocity, the slighter the dependence of f and g upon θ, and the smaller the range of velocities in which $f = g$.

5. If there were no electronic spin, we should have to take, to satisfy the exclusion principle, the orbitally antisymmetric solution for the collision of an electron with a hydrogen atom; and this would lead to a cross section which had a minimum as a function of v. But because of the electron spin the symmetric solution will occur with a third the weight of the antisymmetric one; so that the total first order cross section for atomic hydrogen is

$$(4\pi^2/h^2) \cdot (f^2 + g^2 - fg) \tag{66}$$

Now

$$f^2 + g^2 - fg \geq 3f^2/4 \; ; \; f^2 + g^2 - fg \geq \tfrac{1}{2}(f^2 + g^2) \tag{67}$$

The total cross section can thus never fall much under Born's value, and for low velocities it will be larger. Thus the theory leads to the prediction that atomic hydrogen, and probably the similar alkali atoms, should show no Ramsauer effect.

For other atoms we obtain different results. Thus for helium the orbital wave must be symmetric in two electrons—to correspond to the normal state of the atom—and cannot, by the exclusion principle, be symmetric in all three. The two non-combining wave functions corresponding to (3) turn out to be

$$\text{(a)} \quad \psi(r_1,r_2)X_{\nu\theta\phi}(r_3)+\epsilon\psi(r_1,r_3)X_{\nu\theta\phi}(r_2)+\epsilon^2\psi(r_2,r_3)X_{\nu\theta\phi}(r_1)$$

$$\text{(b)} \quad \psi(r_1,r_2)X_{\nu\theta\phi}(r_3)+\epsilon^2\psi(r_1,r_3)X_{\nu\theta\phi}(r_2)+\epsilon\psi(r_2,r_3)X_{\nu\theta\phi}(r_1)$$

(68)

with
$$\epsilon=\tfrac{1}{2}(i-3^{-1/2})$$

where $\psi(r,r')=\psi(r',r)$ is the wave function for the normal state of the atom.[12]

[12] The functions (68) may be used to compute the excitation probabilities for singlet and triplet atomic states; the final wave functions are for the two cases, e.g. in the system (a)

$$\psi_{\pm}(r_1,\ r_2)\chi_{\nu\theta\phi}(r_3)+\epsilon\psi_{\pm}(r_1,\ r_3)\chi_{\nu\theta\phi}(r_1)+\epsilon^2\psi_{\pm}(r_3,\ r_1)\chi_{\nu\theta\phi}(r_2)$$

with

$$\psi_{\pm}(x,\ y)=\pm\psi_{\pm}(y,\ x)$$

The cross section for the singlets becomes

$$\sigma_+=(4\pi^2/h^2)\left|\int\ \int\ \int dx\,dy\,dz\,\psi_+{}^*(x,\ y)\chi_{\nu\theta\phi}^*(z)\left\{\psi(x,\ y)y_\nu(z)\left[\frac{e^2}{|z-\chi|}\right.\right.\right.$$
$$\left.\left.\left.+\frac{e^2}{|z-y|}-\frac{2e^2}{z}\right]-\psi(y,\ z)\eta_\nu(x)\left[\frac{e^2}{|x-y|}+\frac{e^2}{|x-z|}-\frac{2e^2}{x}\right]\right\}\right|^2$$

That for the triplets is

$$\sigma_-=(12\pi^2/h^2)\left|\int\ \int\ \int dx\,dy\,dz\,\psi_-{}^*(x,\ y)\psi(y,\ z)\chi_{\nu\theta\phi}(z)\eta_\nu(x)\left[\frac{e^2}{|x-y|}+\frac{e^2}{|x-z|}-\frac{2e^2}{x}\right]\right|^2$$

Neither of these vanishes identically. One may obtain a rough idea of the behavior of the cross sections by neglecting the coupling of the atomic electrons, and setting $\psi(x,\ y)=\psi_{100}(x)\ \psi_{100}(y)$,

$$\psi_+(x,\ y)=(1/2^{1/2})\left\{\psi_{100}(x)\psi_{nkm}(y)\pm\psi_{100}(y)\psi_{nkm}(x)\right\}$$

Then

$$\sigma_+=(8\pi^2/h^2)\left|L-\tfrac{1}{2}M-\tfrac{1}{2}N\right|^2;\qquad\sigma_-=(6\pi^2/h^2)\left|M-N\right|^2.$$

with
$$L=\int\ \int dx\,dy\,\psi_{nkm}^*(x)\psi_{100}(x)\chi_{\nu\theta\phi}^*(y)\eta_\nu(y)\ \left[\frac{e^2}{|x-y|}\right]$$

$$M=\int\ \int\ \int dx\,dy\,dz\,\psi_{nkm}^*(x)\ |\ \psi_{100}(y)\ |^2\psi_{100}(z)\chi_{\nu\theta\phi}^*(z)\eta_\nu(x)\ \left[\frac{e^2}{|x-y|}+\frac{e^2}{|x-z|}-\frac{2e^2}{x}\right]$$

$$N=\int\ \int\ \int dx\,dy\,dz\,\psi_{nkm}^*(x)\psi_{100}(y)\psi_{100}^*(x)\psi_{100}(z)\chi_{\nu\theta\phi}^*(z)\eta_\nu(y)\ \left[\frac{e^2}{|x-y|}\right]$$

Here L corresponds to transitions in which one atomic electron is excited; M to those in which one atomic electron is ionized, and the impacting electron is bound in the excited state; N to those in which one atomic electron is freed, and the other excited, and the impacting electron is caught in the normal state. Further

$$L<Av^{-4};\qquad M<Av^{-6};\qquad N<Av^{-8}$$

so that with increasing electronic velocity singlet excitation should predominate.

The first order cross section then is

$$(4\pi^2/h^2) \cdot |f_1 - g_1|^2 \tag{69}$$

with

$$f_1 = \int dr \int dr' \int dr'' |\psi(r,r')|^2 \chi_{\nu\theta\phi}{}^*(r'')\eta_\nu(r'')[-2e^2/r''$$
$$+ e^2/|r''-r'| + e^2/r''-r|] \tag{70}$$

$$g_1 = \int dr \int dr' \int dr'' \psi(r,r')\psi(r,r'')\chi_{\nu\theta\phi}{}^*(r')\eta_\nu(r'')[-2e^2/r''$$
$$+ e^2/|r''-r'| + e^2/|r''-r|]$$

Here again f gives the classical cross section. And since (69) depends upon v and θ much as (7) does, the theory does give, for helium, a break in the monotonic rise of the cross section with decreasing v. In general we can say that the ratio of the true cross section to its "classical" value will pass through a minimum. Whether the cross section itself passes through a minimum, or merely shows a flattening, will depend upon the distribution of zeros of $f(\nu, \theta) - g(\nu, \theta)$. And this effect should occur for all atoms with paired electrons, and should not occur for an atom with an unpaired electron. Thus cadmium should show the break, and sodium should not. But these results are based upon the approximately hydrogenic character of the atomic wave functions, and are thus not directly applicable to molecules.

Since the minimum is more marked for P than for S, for D than for P terms, we should expect the effect to be more marked the higher the azimuthal quantum number of the paired valence electrons. And we should expect the minimum to occur for a lower voltage the higher the azimuthal quantum number

In conclusion it should be recalled that an adequate quantitative treatment of the collision problem involves a more complete solution of the equations (10) than can as yet, even in the simplest case of atomic hydrogen, be given.

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